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Request for grant of a patent

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1. Your reference — C4272(C)/sje

2. Patent application number *(The Patent Office will fill in this part)* — 0228358.8

3. Full name, address and postcode of the or of each applicant *(underline all surnames)* — UNILEVER PLC
UNILEVER HOUSE, BLACKFRIARS
LONDON, EC4P 4BQ

Patents ADP number *(if you know it)* — 50426956002

If the applicant is a corporate body, give the country/state of its incorporation — UNITED KINGDOM

4. Title of the invention — IMPROVEMENTS RELATING TO FABRIC TREATMENT

5. Name of your agent *(if you have one)* — ELLIOTT, Peter William

"Address for Service" in the United Kingdom to which all correspondence should be sent *(including the postcode)* — PATENT DEPARTMENT, UNILEVER PLC
COLWORTH HOUSE, SHARNBROOK
BEDFORD, MK44 1LQ

Patents ADP number *(if you know it)* — 71716220001

6. If you are declaring priority from one or more earlier patent applications, give the country and the date of filing of the or of each of these earlier applications and *(if you know it)* the or each application number

Country	Priority application number *(if you know it)*	Date of filing *(day / month / year)*

7. If this application is divided or otherwise derived from an earlier UK application, give the number and the filing date of the earlier application

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8. Is a statement of inventorship and of right to grant of a patent required in support of this request? *(Answer 'Yes' if:*
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Request for substantive examination *(Patents Form 10/77)*	
Any other documents *(please specify)*	

11. I/We request the grant of a patent on the basis of this application.

Signature(s) Date: **4-Dec-02**

Sandra Jane EDWARDS, Authorised Signatory

12. Name and daytime telephone number of person to contact in the United Kingdom — **Sandra EDWARDS, Tel 01234 22 2068**

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IMPROVEMENTS RELATING TO FABRIC TREATMENT

Technical Field

The present invention relates to Fabric Treatment compositions, and in particular to compositions which contain components which can cross-link with cellulose.

Background of the Invention

Cellulose is a beta 1-4 linked polysaccharide and the principal component of cotton, which is a well-known material for the production of fabrics and in very widespread use. Cellulose is capable of cross-linking by hydrogen bonds which form between the cellulose chains.

The majority of garments purchased world-wide contain at least some cellulose fibres in the form of cotton or rayon and these suffer from the well-known problem that on exposure to water, such as during laundering, fibre dimensions change and cause shrinking and wrinkling of the garments. It is believed that this is due to release and reformation of hydrogen bonds.

So-called 'durable press' treatments of fabrics are intended to overcome these difficulties. One of the most common methods of durable pressing uses a crosslinking agent to immobilise cellulose at a molecular level. Known cross-linking agents include formaldehyde, and urea-glyoxal

resins. Other proposals include epichlorohydrins, vinyl sulphones, triazines, acryloamide and acryloacrylates. None of these proposed technologies have demonstrated real commercial viability to date.

An alternative proposal is to use poly-acids such as BTCA (butyl tetra carboxylic acid) or citric acid as crosslinking agents. These can esterify with the -OH groups of the cellulose to form a covalent cross-link. The covalent cross-link is not disrupted by water and this both prevents deformation of fabrics and assists return to a flat state. One of the difficulties with this approach is that a sodium hypophosphite catalyst is generally used to cause the esterification reaction to proceed and the treated articles require heat curing. Moreover, these poly-acid materials are highly water soluble and are difficult to deposit on fabrics.

A preferred durable press system should be a non-toxic, one component system with low iron-cure times, have some affinity for the fabric surface and not cause fabric strength losses.

Brief Description of the Invention

We have determined that excellent cross-linking benefits can be obtained using a polyester with weak ester bonds which can trans-esterify with cellulose. This is accomplished by forming the polyester between a poly-carboxylic acid and an

alcohol (which term includes phenol) which is a good leaving group.

Accordingly, the present invention provides a method of treating cellulosic materials so as to cause cross-linking which comprises the step of transesterifying the cellulosic material with an effective amount of a polyester wherein said polyester is formed from a polycarboxylic acid and an electron-withdrawing alcohol or imide.

A further aspect of the present invention provides a composition for use in the method described above.

Preferably the method of the present invention further comprises the step of curing the treated materials by ironing.

Detailed Description of the Invention

As noted above, the polyester comprises a polycarboxylic acid esterified with a 'leaving' group which is an alcohol or an imide. The polycarboxylic acid preferably has 2-6 carboxyl groups available for esterification. Most preferably, the polycarboxylic acid has two carbonyl groups available for esterification and typically these are at opposite ends of the polycarboxylic acid. In a preferred embodiment the polyester takes the form:

$$R_1O\text{-}CO\text{-}L\text{-}CO\text{-}OR_2$$

Where R_1O- and -OR_2 are the same or different alcohol residues, and -CO-L-CO- is the residue of the polycarboxylic acid. L is a linking group, which may be substituted, and generally comprises a 2-6 carbon backbone. This form is makes the molecule suitable for cross-linking cellulose chains in cotton.

Polycarboxylic acids:

Preferred polycarboxylic acids include one or more of :

malonic Acid, methylmalonic acid, ethylmalonic acid, butylmalonic acid, dimethylmalonic acid, diethylmalonic acid;

succinic acid, methylsuccinic acid, 2,2-dimethylsuccinic acid, 2-ethyl-2-methylsuccinic acid, 2,3-dimethylsuccinic acid, meso-2,3-dimethylsuccinic acid,

glutaric acid,

2-methylglutaric acid, 3-methylglutaric acid, 2,2-dimethylglutaric acid, 3,3-dimethyl-glutaric acid,

adipic acid, 3-methyladipic acid, 3-tert-butyladipic acid,

pimelic acid,

suberic acid,

azelic acid,

sebacic acid,

1,11-undecanecarboxylic acid, undecanedioic acid, 1,10-decanedicarboxylic acid,

1,12-dodecanedicarboxylic acid,

hexadecanedioic acid,

docosanedioic acid,

tetracosanedioic acid,

tricarballylic acid,
1,2,3,4-butanetetracarboxylic acid,
itaconic acid,
maleic acid,
fumaric acid,
citraconic acid,
mesaconic acid,
trans-glutaconic acid,
trans-beta-hydromuconic acid,
trans-traumatic acid,
trans,trans-muconic acid,
cis-aconitic acid, trans-aconitic acid,
malic acid, citramalic acid,
isopropylmalic acid,
3-hydroxy-3-methylglutaric acid,
tartaric acid,
mucic acid,
citric acid,
dihydroxyfumaric acid,
diglycolic acid,
3,6-dioxaoctanedioic acid,
3,3'-thiodipropionic acid, 3,3'-dithiodipropionic acid,
trans-DL-1,2-cyclopentanedicarboxylic acid,
3,3-tetramethyleneglutaric acid,
camphoric acid,
cyclohexylsuccinic acid,
1,1-cyclohexanediacetic acid,
trans-1,2-cyclohexanedicarboxylic acid,
1,3-cyclohexanedicarboxylic aicd, 1,4-cyclohexanedicarboxylic acid,
1,3,5-cyclohexanetricarboxylic acid,

Kemp's triacid,
1,2,3,4-cyclobutanetetracarboxylic acid,
1,2,3,4,5,6-cyclohexanehexacarboxylic acid
4-Carboxyphenooxyacetic acid,
1,4-phenylenediaectic acid,
1,4-phenylenedipropionic acid,
1,4-phenylenediacrylic acid,
2-Carboxybenzenepropanioc acid,
4,4'-oxybis(benzoic acid),
phthalic acid, isophthalic acid, terephthalic acid,
1,2,3-benzenetricarboxylic acid, 1,3,5-benzenetricarboxylic acid,
1,2,4,5-benzenetetracarboxylic acid,
mellitic acid,
2-methoxyisophthalic acid,
diphenic acid,
4,4'-biphenyldicarboxylic acid,
2,6-Napthalenedicarboxylic acid,
3-carboxy-1,4-dimethyl-2-pyroleacetic acid,

Oligomers (and co-oligomers) of unsaturated carboxylic acids can be used. Suitable materials include oligomers of acrylic acid, methacrylic acid, crotonic acid, vinylacetic acid, 4-pentenoic acid, and/or maleic acid

The acid can comprise a heteroatom. Nitrogen is a preferred heteroatom. Suitable N-containing acids include:
iminodiacetic acid,
3-aminophthalic acid, 2-aminoterephthalic acid, 5-aminoisophthalic acid,
ethylenediamine-N,N'-diacetic acid,

methyliminodiacetic acid,
nitrilotriacetic acid,
ethylenediaminetetraacetic acid,
1,6-diaminohexane-N,N,N',N'-tetraacetic acid,
trans-1,2-diaminocyclohexane-N,N,N',N',-tetraacetic acid,
triethylenetetraminehexaacetic acid,
1,3-diamino-2-hydroxypropane-N,N,N',N'-tetraacetic acid,
ethylenebis(oxyethylenenitrilo)tetraacetic acid,
diethylenetriaminepentaacetic acid,
aspartic acid,
glutamic acid,
2-methylglutamic acid,
2-aminoadipic acid,
3-aminoadipic acid,
2,6-diaminopimelic acid,
cystine
N-benzyliminodiacetic acid,
N-(2-carboxyphenyl)glycine,
2,2'-(ethylenedioxy)dianiline-N,N,N',N'-tetraacetic acid.
porphobilinogen,
4,5-imidazoledicarboxylic acid,
2,2'-bipyridine-4,4'-dicarboxylic acid,
3,4-pyridinedicarboxylic acid, 2,5-pyridinedicarboxylic acid, 3,5-pyridinedicarboxylic acid, 2,6-pyridinedicarboxylic acid,
6-methyl-2,3-pyridinedicarboxylic acid,
2,6-dimethyl-3,5-pyridinedicarboxylic acid

In the case where a nitrogen is present, this may be quaternerised with an appropriate quaternerising agent. Known quaternerising agents include CH_3Cl, CH_3I, and $(CH_3)_2SO_4$.

Alcohols:

Preferred alcohols comprise 5- or 6-membered rings have electron-withdrawing groups in the ortho- and para-positions relative to the alcoholic hydrogen. Examples of such preferred alcohols include N-hydroxysuccinimide and hydroxybenzotriazole. In addition, the alcohol may be in the enol form of a ketone. As noted above, and for the avoidance of doubt, phenols are considered alcohols for the purpose of this specification.

Suitable electron withdrawing substituents on the ring include one or more of : NO_2, CN, CO_2H, CO_2R, CONHR, $CONR_2$, CHO, COR, SO_2R, SO_2OR, SO_2OAr, NO, Ar, $NR_3^{\oplus}$, $SR_2^{\oplus}$, $NH_3^{\oplus}$, F, Cl, Br, I, OAr, SH, SR, OH, OR, $CH=CR_2$. The electron withdrawal can be due to either inductive or resonance effects.

Phenol derivatives with at least one electron-withdrawing substituent are preferred.

Preferred phenol derivatives include:

Vanillan,

Ethyl vanillan,

Eugenol,
isoeuginol,
salicylic acid, ethyl salicylate,
4-cyanophenol,
hydroxyacetophenone,
trichlorophenol,
2,6-dimethoxyphenol,
4-aminophenol (and quaternerised salt),
dimethylaminophenol (and quaternerised salt),
chlorophenol, bromophenol, iodophenol, fluorophenol, dichlorophenol, dibromophenol, diiodophenol, difluorophenol,
hydroxythiophenol,
aminocresol,
4-amino-2,5-dimethylphenol,
6-amino-2,4-dichloro-3-methylphenol,
nitrophenol, dinitrophenol,
hydroxypropiophenone,
2'-hydroxy-5'-methylacetophenone,
5'-chloro-2'-hydroxyacetophenone,
acetovanillone,
4-hydroxybenzaldehyde,
o-vanillan,
4-hydroxy-3-methylbenzaldehyde,
2-chloro-4-hydroxybenzaldehyde,
2-hydroxy-5-methoxybenzaldehyde,
3-ethoxy-4-hydroxybenzaldehyde,
5-nitrovanillan,
3-methoxy-5-nitrosalicyaldehyde,
4-hydroxybenzoic acid,
methylsalicylic acid,
chlorosalicylic acid,

methoxysalicylic acid,
aminosalicylic acid,
methylsalicylic acid,
formylsalicylic acid,
hydroxyisophthalic acid,
methyl hydroxybenzoate,
ethyl hydroxybenzoate,
propyl hydroxybenzoate,
methyl 5-methylsalicylate,
ethyl 5-methylsalicylate,
hydroxybenzamide,
5-chloro-2-hydroxybenzamide,
5-acetylsalicylamide,
2-amino-4-(ethylsulfonyl)phenol

Particularly preferred alcohols include trichlorophenol, isoeuginol, menthol, 4-cyanophenol, ethyl salicylate, 2,6-dimethoxy phenol, 4-aminophenol and dimethylamino phenol. As noted above, imides can also be used as the 'alcohol'. A preferred imide material is N-hydroxysuccinimide.

The alcohol leaving group can have functional properties which give it some utility after the transesterification reaction. One such property is that of a perceptible odour. For example, a notable odour of cloves is obtained with weak isoeuginol esters upon the application of heat (i.e. on ironing). This can act as a useful cue to the user that the reaction is proceeding.

Preferred polyesters include the trichlorophenol diester of succinic acid, the trichlorophenol diester of BTCA, the N-

hydroxysuccinimide diester of succinic acid, the isoeugenol diester of succinic acid, and the menthol diester of succinic acid.

The polyester will typically only have one type of alcohol present, although it is possible to envisage 'mixed' esters in which two or more, different types of alcohol are present.

It is particularly preferred that the polyester has a molecular weight below 1500 Dalton. It is believed that the cellulosic materials will stiffen if larger molecular weight materials are used.

While the polyester can be applied from a non-aqueous solvent (such as THF) it is preferable to apply the material from a wholly or partly aqueous solvent.

Carriers and Product Form:

The compositions of the invention will generally comprise a textile compatible carrier.

In the context of the present invention the term "textile compatible carrier" includes a component which can assist in the interaction of the polyester with the textile. The carrier can also provide benefits in addition to those provided by the first component e.g. softening, cleaning etc. The carrier may be a detergent-active compound or a textile softener or conditioning compound or other suitable detergent or textile treatment agent.

In a washing process, as part of a conventional textile washing product, such as a detergent composition, the textile-compatible carrier will typically be a detergent-active compound. Whereas, if the textile treatment product is a rinse conditioner, the textile-compatible carrier will be a textile softening and/or conditioning compound. These are described in further detail below.

The polyester is preferably used to treat the textile in the wash cycle of a laundering process. The polyester can also be used in the rinse cycle, or applied prior to during ironing.

The composition of the invention may be in the form of a liquid, solid (e.g. powder or tablet), a gel or paste, spray, stick or a foam or mousse. Examples include a soaking product, a rinse treatment (e.g. conditioner or finisher) or a main-wash product. Spray products are particularly suited to application as part of the ironing process.

Liquid compositions may also include an agent which produces a pearlescent appearance, e.g. an organic pearlising compound such as ethylene glycol distearate, or inorganic pearlising pigments such as microfine mica or titanium dioxide (TiO_2) coated mica. Liquid compositions may be in the form of emulsions or emulsion precursors thereof.

Detergent Active Compounds:

If the composition of the present invention is itself in the form of a detergent composition, the textile-compatible carrier may be chosen from soap and non-soap anionic, cationic, nonionic, amphoteric and zwitterionic detergent active compounds, and mixtures thereof.

Many suitable detergent active compounds are available and are fully described in the literature, for example, in "Surface-Active Agents and Detergents", Volumes I and II, by Schwartz, Perry and Berch.

The preferred textile-compatible carriers that can be used are soaps and synthetic non-soap anionic and nonionic compounds.

Anionic surfactants are well-known to those skilled in the art. Examples include alkylbenzene sulphonates, particularly linear alkylbenzene sulphonates having an alkyl chain length of C_8-C_{15}; primary and secondary alkylsulphates, particularly C_8-C_{15} primary alkyl sulphates; alkyl ether sulphates; olefin sulphonates; alkyl xylene sulphonates; dialkyl sulphosuccinates; and fatty acid ester sulphonates. Sodium salts are generally preferred.

Nonionic surfactants that may be used include the primary and secondary alcohol ethoxylates, especially the C_8-C_{20} aliphatic alcohols ethoxylated with an average of from 1 to

20 moles of ethylene oxide per mole of alcohol, and more especially the C_{10}-C_{15} primary and secondary aliphatic alcohols ethoxylated with an average of from 1 to 10 moles of ethylene oxide per mole of alcohol. Non-ethoxylated nonionic surfactants include alkylpolyglycosides, glycerol monoethers, and polyhydroxyamides (glucamide).

Cationic surfactants that may be used include quaternary ammonium salts of the general formula $R_1R_2R_3R_4N^+ X^-$ wherein the R groups are independently hydrocarbyl chains of C_1-C_{22} length, typically alkyl, hydroxyalkyl or ethoxylated alkyl groups, and X is a solubilising cation (for example, compounds in which R_1 is a C_8-C_{22} alkyl group, preferably a C_8-C_{10} or C_{12}-C_{14} alkyl group, R_2 is a methyl group, and R_3 and R_4, which may be the same or different, are methyl or hydroxyethyl groups); and cationic esters (for example, choline esters) and pyridinium salts.

The total quantity of detergent surfactant in the composition is suitably from 0.1 to 60 wt% e.g. 0.5-55 wt%, such as 5-50wt%.

Preferably, the quantity of anionic surfactant (when present) is in the range of from 1 to 50% by weight of the total composition. More preferably, the quantity of anionic surfactant is in the range of from 3 to 35% by weight, e.g. 5 to 30% by weight.

Preferably, the quantity of nonionic surfactant when present is in the range of from 2 to 25% by weight, more preferably from 5 to 20% by weight.

Amphoteric surfactants may also be used, for example amine oxides or betaines.

Builders:

The compositions may suitably contain from 10 to 70%, preferably from 15 to 70% by weight, of detergency builder. Preferably, the quantity of builder is in the range of from 15 to 50% by weight.

The detergent composition may contain as builder a crystalline aluminosilicate, preferably an alkali metal aluminosilicate, more preferably a sodium aluminosilicate.

The aluminosilicate may generally be incorporated in amounts of from 10 to 70% by weight (anhydrous basis), preferably from 25 to 50%. Aluminosilicates are materials having the general formula:

$$0.8\text{-}1.5\ M_2O.\ \ Al_2O_3.\ \ 0.8\text{-}6\ \ SiO_2$$

where M is a monovalent cation, preferably sodium. These materials contain some bound water and are required to have a calcium ion exchange capacity of at least 50 mg CaO/g. The preferred sodium aluminosilicates contain 1.5-3.5 SiO_2 units in the formula above. They can be prepared readily by

reaction between sodium silicate and sodium aluminate, as amply described in the literature.

Alternatively, or additionally to the aluminosilicate builders, phosphate builders may be used.

Textile Softening and/or Conditioner Compounds:

If the composition of the present invention is in the form of a textile conditioner composition, the textile-compatible carrier will be a textile softening and/or conditioning compound (hereinafter referred to as "textile softening compound"), which may be a cationic or nonionic compound.

The softening and/or conditioning compounds may be water insoluble quaternary ammonium compounds. The compounds may be present in amounts of up to 8% by weight (based on the total amount of the composition) in which case the compositions are considered dilute, or at levels from 8% to about 50% by weight, in which case the compositions are considered concentrates.

Compositions suitable for delivery during the rinse cycle may also be delivered to the textile in the tumble dryer if used in a suitable form. Thus, another product form is a composition (for example, a paste) suitable for coating onto, and delivery from, a substrate e.g. a flexible sheet or sponge or a suitable dispenser during a tumble dryer cycle.

Suitable cationic textile softening compounds are substantially water-insoluble quaternary ammonium materials comprising a single alkyl or alkenyl long chain having an average chain length greater than or equal to C_{20}. More preferably, softening compounds comprise a polar head group and two alkyl or alkenyl chains having an average chain length greater than or equal to C_{14}. Preferably the textile softening compounds have two, long-chain, alkyl or alkenyl chains each having an average chain length greater than or equal to C_{16}.

Most preferably at least 50% of the long chain alkyl or alkenyl groups have a chain length of C_{18} or above. It is preferred if the long chain alkyl or alkenyl groups of the textile softening compound are predominantly linear.

Quaternary ammonium compounds having two long-chain aliphatic groups, for example, distearyldimethyl ammonium chloride and di(hardened tallow alkyl) dimethyl ammonium chloride, are widely used in commercially available rinse conditioner compositions. Other examples of these cationic compounds are to be found in "Surface-Active Agents and Detergents", Volumes I and II, by Schwartz, Perry and Berch. Any of the conventional types of such compounds may be used in the compositions of the present invention.

The textile softening compounds are preferably compounds that provide excellent softening, and are characterised by a chain melting Lβ to Lα transition temperature greater than

25°C, preferably greater than 35°C, most preferably greater than 45°C. This Lβ to Lα transition can be measured by DSC as defined in "Handbook of Lipid Bilayers", D Marsh, CRC Press, Boca Raton, Florida, 1990 (pages 137 and 337).

Substantially water-insoluble textile softening compounds are defined as textile softening compounds having a solubility of less than 1×10^{-3} wt % in demineralised water at 20°C. Preferably the textile softening compounds have a solubility of less than 1×10^{-4} wt%, more preferably less than 1×10^{-8} to 1×10^{-6} wt%.

Especially preferred are cationic textile softening compounds that are water-insoluble quaternary ammonium materials having two C_{12-22} alkyl or alkenyl groups connected to the molecule via at least one ester link, preferably two ester links. Di(tallowoxyloxyethyl) dimethyl ammonium chloride and/or its hardened tallow analogue are especially preferred of the compounds of this type. Other preferred materials include 1,2-bis(hardened tallowoyloxy)-3-trimethylammonium propane chloride. Their methods of preparation are, for example, described in US 4 137 180 (Lever Brothers Co). Preferably these materials comprise small amounts of the corresponding monoester as described in US 4 137 180, for example, 1-hardened tallowoyloxy-2-hydroxy-3-trimethylammonium propane chloride.

Other useful cationic softening agents are alkyl pyridinium salts and substituted imidazoline species. Also useful are

primary, secondary and tertiary amines and the condensation products of fatty acids with alkylpolyamines.

The compositions may alternatively or additionally contain water-soluble cationic textile softeners, as described in GB 2 039 556B (Unilever).

The compositions may comprise a cationic textile softening compound and an oil, for example as disclosed in EP-A-0829531.

The compositions may alternatively or additionally contain nonionic textile softening agents such as lanolin and derivatives thereof.

Lecithins are also suitable softening compounds.

Nonionic softeners include Lβ phase forming sugar esters (as described in M Hato et al Langmuir 12, 1659, 1666, (1996)) and related materials such as glycerol monostearate or sorbitan esters. Often these materials are used in conjunction with cationic materials to assist deposition (see, for example, GB 2 202 244). Silicones are used in a similar way as a co-softener with a cationic softener in rinse treatments (see, for example, GB 1 549 180).

The compositions may also suitably contain a nonionic stabilising agent. Suitable nonionic stabilising agents are linear C_8 to C_{22} alcohols alkoxylated with 10 to 20 moles of alkylene oxide, C_{10} to C_{20} alcohols, or mixtures thereof.

Advantageously the nonionic stabilising agent is a linear C_8 to C_{22} alcohol alkoxylated with 10 to 20 moles of alkylene oxide. Preferably, the level of nonionic stabiliser is within the range from 0.1 to 10% by weight, more preferably from 0.5 to 5% by weight, most preferably from 1 to 4% by weight. The mole ratio of the quaternary ammonium compound and/or other cationic softening agent to the nonionic stabilising agent is suitably within the range from 40:1 to about 1:1, preferably within the range from 18:1 to about 3:1.

The composition can also contain fatty acids, for example C_8 to C_{24} alkyl or alkenyl monocarboxylic acids or polymers thereof. Preferably saturated fatty acids are used, in particular, hardened tallow C_{16} to C_{18} fatty acids. Preferably the fatty acid is non-saponified, more preferably the fatty acid is free, for example oleic acid, lauric acid or tallow fatty acid. The level of fatty acid material is preferably more than 0.1% by weight, more preferably more than 0.2% by weight. Concentrated compositions may comprise from 0.5 to 20% by weight of fatty acid, more preferably 1% to 10% by weight. The weight ratio of quaternary ammonium material or other cationic softening agent to fatty acid material is preferably from 10:1 to 1:10.

Other Components

Compositions according to the invention may comprise soil release polymers such as block copolymers of polyethylene oxide and terephthalate.

Other optional ingredients include emulsifiers, electrolytes (for example, sodium chloride or calcium chloride) preferably in the range from 0.01 to 5% by weight, pH buffering agents, and perfumes (preferably from 0.1 to 5% by weight).

Further optional ingredients include non-aqueous solvents,, fluorescers, colourants, hydrotropes, antifoaming agents, enzymes, optical brightening agents, and opacifiers.

Suitable bleaches include peroxygen bleaches. Inorganic peroxygen bleaching agents, such as perborates and percarbonates are preferably combined with bleach activators. Where inorganic peroxygen bleaching agents are present the nonanoyloxybenzene sulphonate (NOBS) and tetra-acetyl ethylene diamine (TAED) activators are typical and preferred.

Suitable enzymes include proteases, amylases, lipases, cellulases, peroxidases and mixtures thereof.

In addition, compositions may comprise one or more of anti-shrinking agents, anti-wrinkle agents, anti-spotting agents, germicides, fungicides, anti-oxidants, UV absorbers (sunscreens), heavy metal sequestrants, chlorine scavengers,

dye fixatives, anti-corrosion agents, drape imparting agents, antistatic agents and ironing aids. The lists of optional components are not intended to be exhaustive.

In order that the invention may be further and better understood it will be described below with reference to several non-limiting examples.

Examples

In the examples given below, the synthesised esters were pad applied to oxford cotton fabric (18x6cm) at 100% pick-up from solvent (e.g. THF and/or water). The fabric swatches were then dried, followed by an iron cure on high setting (cotton/linen) for the time specified.

After curing, the swatches were conditioned at 20°C, 65% relative humidity then the crease recovery angle (CRA) measured (using BS1553086). A sample of fabric (25mmx50mm) was folded in half forming a sharp crease and held under a weight of 1kg for 1 minute. On releasing the sample the crease opens up to a certain degree. After 1 minute relaxation, time the angle is measured. The fabric is tested in the warp direction only (hence maximum CRA is 180°). Higher CRA therefore indicates less wrinkled fabric.

Example 1: 2,4,6-Trichlorophenol Diester of Butanetetracarboxylic Acid

Butane tetracarboxylic acid (BTCA) (20.84g, 0.089mol) and 2,4,6-trichlorophenol (35.80g, 0.18mol) were weighed into a RB flask (250cm^3). Nitrogen was flushed through the flask for 15 minutes, then distilled THF (150cm^3) was added. After stirring under nitrogen for 30 minutes, diisopropylcarbodiimide (29.0cm^3, 0.18mol) was added dropwise over 20 minutes. The reaction was allowed to stir overnight under nitrogen. The mixture was filtered, washed with THF then stirred for one hour to ensure that formation of precipitate was complete. The solvent was removed to afford the crude product. This was washed several times with dichoromethane to yield the product upon removal of the solvent from the filtrate.

CRA results obtained with a 5% solution of diester in THF (1g diester in 19g THF) are shown in Table 1 below.

Table 1

	CRA			
	10s iron	20s iron	30s iron	60s iron
UT Control	79	-	-	-
5% Diester	92	99	98	103

From these results it can be seen that less creasing (higher CRA) was obtained with the treated samples than with the

untreated samples (UT). It can also be seen that the effect of a longer ironing-time on treated swatches is to further improve the results for the crease test (which occurs after the ironing step).

Example 2: 2,4,5-Trichlorophenol Diester of Succinic Acid

Succinic acid (1.5g, 0.013mol) was dissolved in DMSO ($50cm^3$). 1,1'-Carbonyldiimidazole (5.0g, 0.03mol) was added and the mixture stirred for 30mins at room temperature. 2,4,5-Trichlorophenol (5.05g, 0.026mol) was then added and the mixture stirred at room temperature overnight. The mixture was added to water, filtered, then washed with water followed by diethyl ether to yield a white solid (2.03g, 33%) δ_H (500 MHz; $CDCl_3$) 3.07 (4H, s, CH_2-CH_2-C(O)-O-) and 7.55 & 7.29 (4H, s, *Ph*).

CRA results obtained with a 7.65% solution of diester in THF are given in Table 2 below:

Table 2

	CRA			
	10s iron	20s iron	30s iron	60s iron
UT Control	78	-	-	-
7.65% Diester	92	99	102	113

From these results it can again be seen that less creasing (higher CRA) was obtained with the treated samples than with the untreated samples (UT), and that a longer curing step further improved the results.

Example 3: N-Hydroxysuccinimide Diester of Succinic Acid

Succinic acid (2.0g, 0.017mol) was dissolved in THF (50cm^3). 1,1'-Carbonyldiimidazole (5.49g, 0.034mol) was added and the mixture stirred for 30mins at room temperature. N-Hydroxysuccinimide (3.89g, 0.034mol) was added and the mixture stirred at room temperature overnight. The mixture was added to water, filtered, then washed with water then diethyl ether to yield a white solid (2.0g, 38%)

δ_H (500 MHz; $CDCl_3$) 2.59 (8H, s, CH_2-CH_2-CO-N-) and 2.89 (4H, s, CH_2-CH_2-C(O)-O-)

CRA results obtained with a 5.25% solution of diester in THF and water are given in Table 3 below:

Table 3

	CRA			
	10s iron	20s iron	30s iron	60s iron
UT Control	71			
5.25% Diester (THF)	87	88	93	95
5.25% Diester (water)	93	95	92	92

From these results it can be seen that less creasing (higher CRA) was obtained with the treated samples (both from THF and water) than with the untreated samples (UT). A water carrier gives good results with both a short and long a short curing/ironing step.

Example 4: Vanillan Diester of Succinic Acid

(1) Organic solvent method:

Vanillin (9.82 g, 64.5 mMols) was dissolved in anhydrous THF (100 cm^3) with stirring at room temperature and under nitrogen. Anhydrous sodium carbonate (8.2 g, 77.4 mMols, 1.2 equiv) was then added and stirring was continued for 30 mins. Succinyl chloride (5 g, 32.25 mMols, 0.5 equiv) was then added dropwise to the slurry over 20 mins, the mixture was then stirred in the dark for a further 18 hours. The mixture was then filtered and the solvent removed from the filtrate under reduced pressure to give an off-white solid. The crude product was then recrystallised from IPA to give a white solid (2.7 g, 24 %). δ_H (500 MHz; $CDCl_3$) 3.08 (2H, s, *-CH_2-C(O)-O-*), 3.89 (3H, s, *-OCH_3*), 7.27 – 7.50 (3H, m, *Ph*) and 9.95 (1H, s, *-CHO*).

(2) Schotten-Baumann method:

Sodium Hydroxide (1.3 g, 32.5 mmols) was dissolved in distilled water (100 cm^3). To this solution vanillin (4.91

g, 32.5 mmols) was added and the solution was stirred to give a light yellow solution. The solution was then cooled to 0 °C prior to the dropwise addition of succinyl chloride (2.5 g, 16.25 mmols). The mixture was then allowed to warm to room temperature and stirring was continued for a further 10 mins to give a light yellow precipitate. The mixture was then poured into water (200 cm^3) and stirred at room temperature for 30 mins. The solution was filtered and the solid material retained. This crude product was then recrystallised to give a white solid (0.84 g, 13 %).

CRA results obtained with 6.55% Diester in THF (19cm^3) initially, increasing amount of water added are given in Table 4 below:

Table 4

	CRA - 60s Iron
UT Control	77
6.55% Diester in THF (no water added)	82
6.55% Diester in THF + 1cm^3 H_2O	86
6.55% Diester in THF + 2cm^3 H_2O	85
6.55% Diester in THF + 3cm^3 H_2O	88
6.55% Diester in THF + 5cm^3 H_2O	91

From these results it can be seen that less creasing (higher CRA) was obtained with the treated samples (both from THF and THF+water) than with the untreated samples (UT).

Example 5: 4-Cyanophenol Diester of Succinic Acid

4-Cyanophenol (7.7 g, 64.5 mMols) was dissolved in anhydrous THF (100 cm^3) with stirring at room temperature and under nitrogen. Anhydrous sodium carbonate (8.2 g, 77.4 mMols, 1.2 equivalents) was then added and stirring was continued for a further 10 mins. Succinyl chloride was then added dropwise over 20 mins and the mixture was stirred under nitrogen for a further 18 hours in the dark. The grey slurry was filtered and the solvent was removed from the filtrate under reduced pressure to give a grey solid. This crude material was then recrystallised from IPA to give a off-white solid (3.7 g, 36 %). δ_H (500 MHz; $CDCl_3$) 3.03 (2H, s, $-CH_2-C(O)-O-$), 7.24 (2 H, d, J 8, Ph). & 7.69 (2 H, d, J 8.5, Ph).

CRA results obtained with a 5.45% solution of diester in THF are given in Table 5 below:

Table 5

	CRA - 60s Iron
UT Control	77
5.45% Diester	84

From these results it can be seen that less creasing (higher CRA) was obtained with the treated samples than with the untreated samples (UT).

Example 6: Isoeuginol Diester of Succinic Acid

Isoeuginaol (25g, 0.15mol) was dissolved in THF ($100cm^3$). Sodium carbonate (16.14g, 0.15mol) was added and the mixture stirred at room temperature. Succinyl chloride (11.8g, 0.075mol) was added to the stirred mixture over 20 minutes, and the mixture stirred for a further 90 minutes. The reaction mixture was then heated to $50^{\circ}C$ for 60 mins, then stirred at room temperature overnight. The mixture was filtered and the solvent removed under reduced pressure to give a dark coloured oil which solidified upon standing. This crude material was recrystallised from ethyl acetate and diethyl ether to give an off-white solid (4.67g, 8%) δ_H (500 MHz; $CDCl_3$) 1.86 (6H, d, $-CH_3$-CH=CH-), 3.80 (6H, s, Ph CH_3), 6.34 - 6.14(4H, m, CH=$CH$$CH_3$) and 6.70-6.88(6H, m, *Ph*).

Upon application of the isoeuginol diester to cotton and subsequent ironing, a clove fragrance was released as the trans-esterification crosslinking occurred.

CLAIMS

1. A method of treating cellulosic materials so as to cause cross-linking which comprises the step of transesterifying the cellulosic material with an effective amount of a polyester wherein said polyester is formed from a polycarboxylic acid and an electron-withdrawing alcohol or imide.

2. A method according to claim 1 which further comprises the step of heat curing the materials.

3. A composition for use in the method of claim one which comprises an effective amount of a polyester is formed from a polycarboxylic acid and an electron-withdrawing alcohol or imide..

4. A composition according to claim 3 wherein the polycarboxylic acid is succinic acid, butyl tetra carboxylic acid (BTCA), 3,6-dioxaoctanedioic acid, tartaric acid, mucic acid, glutamic acid, methylamino diacetic acid, or nitriloacetic acid.

5. A composition according to claim 3 wherein the alcohol or imide is trichlorophenol, isoeuginol, menthol, 4-cyanophenol, ethyl salicylate, 2,6-dimethoxy phenol, 4-aminophenol, dimethylamino phenol or N-hydroxysuccinimide.

6. A composition according to claim 3 wherein the alcohol is odiferous.

7. A composition according to claim 3 wherein the polyesters is the trichlorophenol diester of succinic acid, the trichlorophenol diester of BTCA, the N-hydroxysuccinimide diester of succinic acid, the isoeugenol diester of succinic acid or the menthol diester of succinic acid.

8. A composition accord to claim 3 wherein the polyester has a molecular weight below 1500 Dalton.

9. A composition according to claim 3 further comprising a textile compatible carrier.

10. A composition according to claim 9 wherein the textile compatible carrier comprises a surfactant.